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AUTHOR(S):

Hashimoto, Takahiro; Ota, Yuichi; Yamamoto, Haruyoshi Q.; Suzuki, Yuya; Shimojima, Takahiro; Watanabe, Shuntaro; Chen, Chuangtian; ... Shibauchi, Takasada; Okazaki, Kozo; Shin, Shik

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ARTICLE

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Superconducting gap anisotropy sensitive to nematic domains in FeSe

Takahiro Hashimoto¹, Yuichi Ota¹, Haruyoshi Q. Yamamoto¹, Yuya Suzuki², Takahiro Shimojima², Shuntaro Watanabe³, Chuangtian Chen⁴, Shigeru Kasahara⁵, Yuji Matsuda⁵, Takasada Shibauchi⁶, Kozo Okazaki¹ & Shik Shin¹

The structure of the superconducting gap in unconventional superconductors holds a key to understand the momentum-dependent pairing interactions. In superconducting FeSe, there have been controversial results reporting nodal and nodeless gap structures, raising a fundamental issue of pairing mechanisms of iron-based superconductivity. Here, by utilizing polarization-dependent laser-excited angle-resolved photoemission spectroscopy, we report a detailed momentum dependence of the gap in single- and multi-domain regions of orthorhombic FeSe crystals. We confirm that the superconducting gap has a twofold in-plane anisotropy, associated with the nematicity due to orbital ordering. In twinned regions, we clearly find finite gap minima near the vertices of the major axis of the elliptical zone-centered Fermi surface, indicating a nodeless state. In contrast, the single-domain gap drops steeply to zero in a narrow angle range, evidencing for nascent nodes. Such unusual node lifting in multi-domain regions can be explained by the nematicity-induced time-reversal symmetry breaking near the twin boundaries.

¹Institute for Solid State Physics (ISSP), University of Tokyo, Kashiwa, Chiba 277-8581, Japan. ²Quantum-Phase Electronics Center (QPEC) and Department of Applied Physics University of Tokyo, Bunkyo, Tokyo 113-8656, Japan. ³Research Institute for Science and Technology Tokyo University of Science, Chiba 278-8510, Japan. ⁴Beijing Center for Crystal R&D Chinese Academy of Science (CAS) Zhongguancun, Beijing 100190, China. ⁵Department of Physics, Kyoto University, Kyoto 606-8502, Japan. ⁶Department of Advanced Materials Science, University of Tokyo, Kashiwa, Chiba 277-8561, Japan. Correspondence and requests for materials should be addressed to K.O. (email: okazaki@issp.u-tokyo.ac.jp) or to S.S. (email: shin@issp.u-tokyo.ac.jp)

Since the discovery of Fe-based superconductors¹, they have been actively investigated to fully understand their superconducting (SC) mechanisms. Among the several kinds of Fe-based superconductors discovered so far, FeSe has the simplest crystal structure consisting only of SC layers². After high-quality single crystals grown by the vapor transport method became available³, intrinsic properties of FeSe have attracted much attention. One of the noticeable properties of FeSe is its SC transition temperature (T_c). While T_c of bulk FeSe is ~ 10 K at ambient pressure⁴ and it increases to 37 K under applied pressure of 9 GPa⁵, it has been reported that superconductivity above 100 K is observed for single-layer FeSe grown on SrTiO₃⁶. Another prominent feature of FeSe is its small Fermi energy (ϵ_F), and thus, FeSe has been proposed to be in the crossover regime between weakly coupled Bardeen–Cooper–Schrieffer (BCS) and strongly coupled Bose–Einstein–condensate (BEC) limits⁴, where ϵ_F is comparable to the SC gap, as well as the bands around the Γ point of FeSe_{1-x}Te_x^{7,8}.

The other features that may be directly related to the mechanism of superconductivity in FeSe are the existence of the structural transition from the tetragonal phase to the orthorhombic phase at $T_s \sim 90$ K and the absence of the anti-ferromagnetic ordering⁹ unlike other Fe-based superconductors. It has been discussed based on the angle-resolved photoemission spectroscopy (ARPES) measurements^{10–14} that the structural transition is accompanied by orbital ordering. They reported that the splitting of the Fe $3d_{yz}$ and $3d_{zx}$ bands emerges at the M point around T_s and it increases as large as 50 meV. This large splitting has been considered to be too large for the crystal field splitting due to the structural transition, and thus regarded as the evidence of an electronically driven orbital ordering. On the other hand, however, several recent reports have interpreted this splitting as that of $3d_{yz/zx}$ and $3d_{xy}$ ^{15,16}, or that due to the spin–orbit

coupling¹⁷. At the Γ point, it has been confirmed that the $3d_{yz}$ and $3d_{zx}$ bands split, and one of the bands sinks below E_F and the other forms an elliptical hole Fermi surface (FS) by ARPES on the detwinned FeSe¹⁸. Similar inequivalent electron occupation of the Fe $3d_{yz}$ and $3d_{zx}$ orbitals has been observed by ARPES in Ba(Fe, Co)₂As₂¹⁹ and NaFeAs^{20,21}. However, the interplay of this band splitting accompanied with the orbital ordering and superconductivity is still elusive. Revealing the SC gap anisotropy of the elliptical FS at the Γ point of FeSe should be crucial for understanding the role of the orbital ordering in superconductivity. In addition, the existence of line nodes in the SC gap of FeSe has been suggested from the thermal conductivity and scanning tunneling microscopy/spectroscopy (STM/STS) measurements⁴, although some reports suggest a fully gapped state without nodes^{22–25}. Determination of the positions of the SC gap nodes is important for clarifying the SC mechanism.

In this paper, a study on the SC gap anisotropy of the zone-centered hole FS is presented based on the laser-excited ARPES measurements^{26,27} of single-crystal FeSe. We observe that the fourfold symmetry is significantly broken in the SC gap anisotropy, which is considered to be due to the orbital ordering, and find that while the SC gap node is not observed for multi-domain samples, it exists at the vertices of the major axis of the elliptical FS for single-domain samples. This can be attributed to breaking of time-reversal symmetry at the twin boundaries and our results reveal the effects of time-reversal symmetry breaking on the nodal SC gap anisotropy.

Results

Fermi surfaces and band dispersions of the twinned FeSe.

Figure 1c and f shows the FS maps at the Brillouin-zone (BZ) center measured at 15 K ($>T_c$), taken with p - and s -polarized

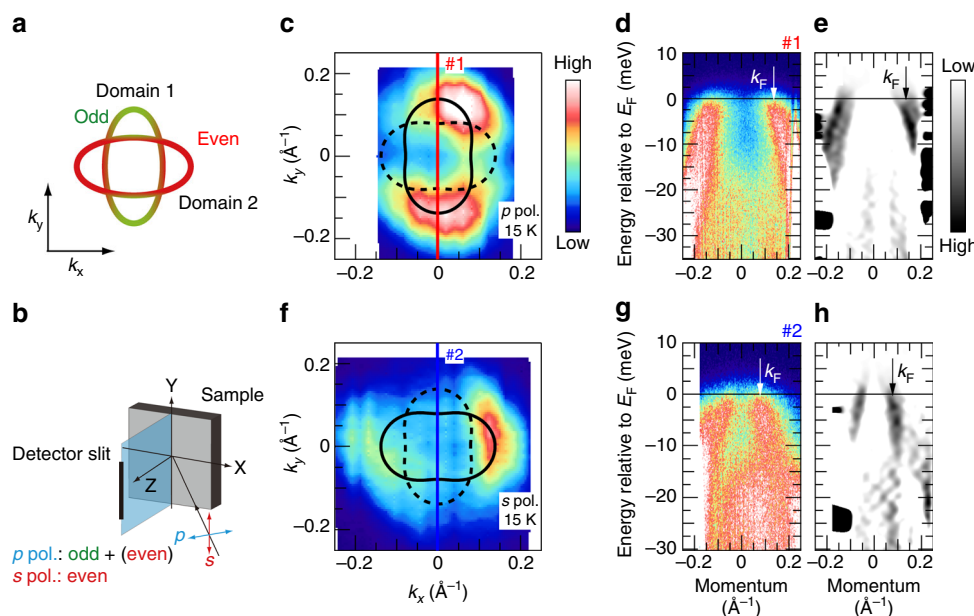


Fig. 1 Electronic structure of the twinned FeSe at 15 K in the orbital ordered state. **a** Schematic FSs at the zone center. x and y are coordinates along the crystal axes of the orthorhombic setting. Due to the orbital ordering, two elliptical FSs are overlapped. Portions of the orbital contributions in those FSs are indicated by red and green for even and odd parity with respect to the mirror plane defined in **b**, respectively. **b** Experimental configuration. A mirror plane is defined to be parallel to the detector slit. Definition of p - and s -polarized light and sample axes is shown. **c** Plots of the ARPES intensity at E_F as a function of the two-dimensional wavevector measured with p -polarized light. The intensity is obtained by integrating the spectra within ± 3 meV with respect to E_F . The experimental FS (solid ellipse) and a duplicate rotated by 90° caused by twin domains (dashed ellipse) are shown. **d** ARPES intensity plot, **e** momentum second derivative of **d** at #1 in **c**. The arrow indicates a k_F position. **f–h** The same as **c–e** but taken with s -polarized light reflecting the other domain

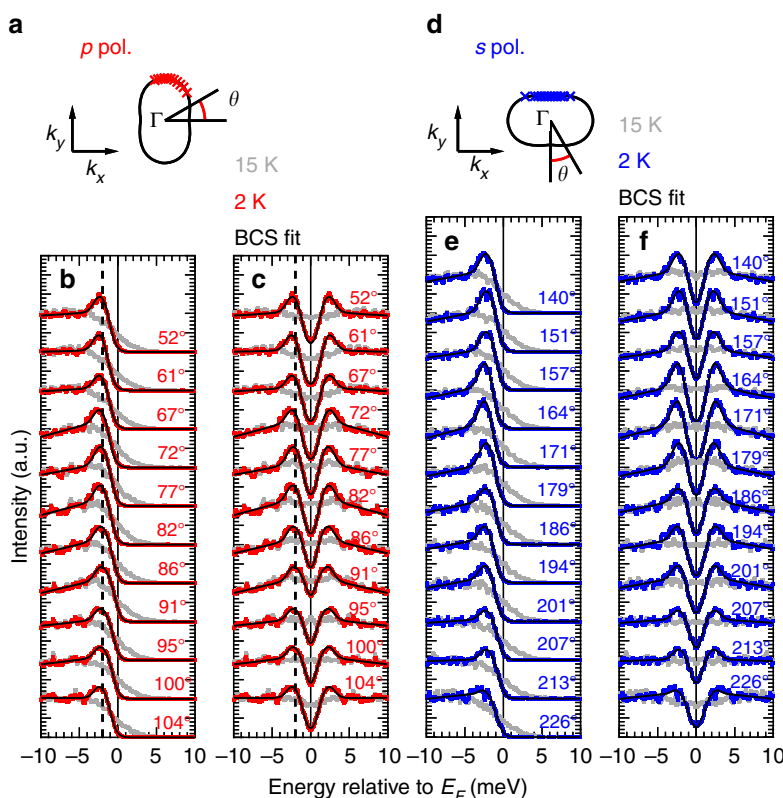


Fig. 2 Superconducting gap anisotropy of twinned FeSe. **a** Definition of FS angle in case of *p*-polarized light. Red points indicate the k_F positions where energy distribution curves (EDCs) in **b** and **c** are taken. **b** EDCs at various k_F points along the FS at 15 K (gray) and 2 K (red). Black lines show the fits to the BCS fitting function. FS angle defined in **a** is shown for each EDC. **c** The same as **b** but symmetrized with respect to E_F . **d-f** The same as **a-c** but taken with *s*-polarized light

incident light. Two FSs were observed and their shapes were twofold symmetric and elliptical. They are rotated to each other by 90° and elongated along the k_y and k_x directions, respectively. Photoemission intensity of the FS elongated along the k_y (k_x) direction was higher for *p*-(*s*-) polarization. Below T_c , the crystal symmetry is transformed from the tetragonal phase to the orthorhombic phase, and therefore, the formation of structural twins is generally inevitable. Observed polarization dependence can be explained by the orbital character of these two FSs due to twinning. Each Fe 3*d* orbital can be classified into even or odd parity with regard to the mirror plane which is parallel to the detector slit (see Supplementary Fig. 1 and Supplementary Note 1 for details). Due to the parity selection rule, *p*- (*s*-) polarized light predominantly observes orbital with odd (even) parity. Considering orbital components of the FS determined by the previous work¹⁸, the FS of two domains can be selectively observed by *p*- (*s*-) polarized light as shown in Fig. 1c, f. Figure 1d and g shows energy-momentum (*E-k*) images in cut #1 in Fig. 1c and cut #2 in Fig. 1f taken with *p*- and *s*-polarized light, respectively. Figure 1e and h are their momentum second derivatives. One can see that a hole band crosses the Fermi level (E_F) at different Fermi wavevector k_F positions for each polarization. The different k_F positions of the observed bands correspond to those of the major and minor axes of the elliptical FS. The k_F positions are determined from momentum distribution curves (MDCs) at E_F (see Supplementary Fig. 6 and Supplementary Note 6 for details).

SC gap structure of the twinned FeSe. Figure 2b and e shows the energy distribution curves (EDCs) at k_F below T_c and above T_c taken with *p*- and *s*-polarized light, respectively. Each EDC is

identified with a FS angle θ , and the k_F positions are shown in Fig. 2a, d. To cancel out the effect of the Fermi-Dirac cutoff, the EDCs were symmetrized with respect to E_F , and the results are shown in Fig. 2c, f. Sharp SC coherence peaks can be recognized very clearly in the spectra below T_c . The vertical dashed line in Fig. 2c indicates the peak position of the EDC at $\theta = 91^\circ$, which is at the end of the major axis of the elliptical FS. The EDC at $\theta = 61^\circ$, for example, has a higher peak energy, indicating a finite SC gap anisotropy. Previous STM/STS measurements reported a two-peak structure⁴ indicating two SC gaps ($\Delta \sim 2.5$ and 3.5 meV). Current results correspond to the smaller gap, and the larger gap may exist at the zone corner. In order to quantify the SC gap sizes, we fitted the spectra to the BCS spectral function and the results are shown as solid lines (see Supplementary Note 7 for details of the fitting function). The observed spectra are well reproduced by the fitting function, indicating reliability of the obtained SC gap sizes.

SC structure of single-domain FeSe. Figure 3 shows the results for another sample, which has a different intensity ratio between two polarizations from Fig. 1. The observed FSs are shown in Fig. 3a, b. The intensity of the FS observed by *s*-polarized light is much weaker compared to that by *p*-polarized light, and this intensity difference is similar to that of the detwinned sample (Supplementary Fig. 2 and Supplementary Note 2). By contrast, Fig. 1c, f shows similar intensity of the FS between *s*- and *p*-polarized light. Considering this difference, the results shown in Fig. 3 can be interpreted as observation of the single-domain region, although any intentional uniaxial tensile strain was not applied to the sample. This is probably owing to the small laser

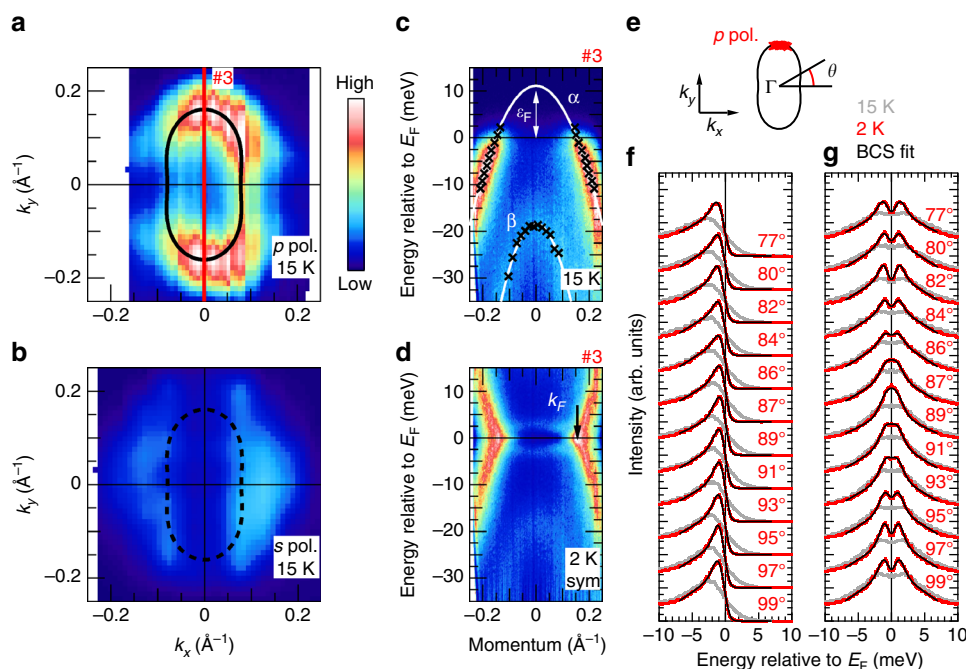


Fig. 3 Superconducting gap anisotropy of single-domain FeSe without uniaxial tensile strain. **a** Plots of the ARPES intensity at E_F of FeSe as a function of the two-dimensional wavevector measured with p -polarized light. The intensity is obtained by integrating the spectra within 3 meV with respect to E_F . Black ellipse indicates the experimental FS. **b** The same as **a** but measured with s -polarized light. **c** ARPES intensity plot above T_c (15 K) at the momentum line shown in **a**, taken with p -polarized light. Black markers represent the experimental band dispersion determined from momentum distribution curves and energy distribution curves (EDCs) for the α and β band. The Fermi energy E_F is shown for the α band. **d** The same as **c** but taken below T_c (2 K) and the data are symmetrized with respect to E_F . The black arrow indicates the k_F position. **e** Definition of θ angle. The red points indicate the k_F values where EDCs in **f** and **g** are taken. **f** EDCs at different k_F values along the FS at 15 K (gray) and 2 K (red). Black lines show the fits to the BCS fitting function. The FS angles defined in **e** are shown for each EDC. **g** Same as **f** but symmetrized at E_F .

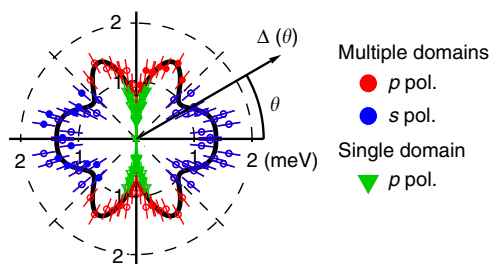


Fig. 4 Superconducting gap anisotropy of the elliptical Fermi surface. Results of the multi-domain sample with p - (red circle) and s - (blue circle) polarized light are shown together, considering that each polarization predominantly probes different domains. Results of the single-domain sample (green triangle) are also shown together. Solid symbols are obtained from BCS spectra fitting and open symbols are symmetrized by taking into account the orthorhombic crystal symmetry. Error bars are determined by the systematic and statistical error of the calibrated E_F positions, as explained in Supplementary Note 8. The black curve is fitting to the observed anisotropy of the multi-domain sample, considering the twofold orthorhombic symmetry. The fitting function is $\Delta(\theta) = |A + B \cos(2\theta) + C \cos(4\theta) + D \cos(6\theta) + E \cos(8\theta)|$.

spot size ($\sim 200 \mu\text{m}$) and the large domain size of the cleaved surface (see Supplementary Fig. 5 and Supplementary Note 5 for the position dependence of the spectra). Similar results for the observation of the single-domain region have been reported for FeSe by Raman scattering²⁸ and ARPES²⁹.

The clear image in Fig. 3c enables a discussion about the band dispersions. The value of k_z for the present results obtained with 7-eV laser can be estimated from the position of the β band,

which lies below E_F as shown in Fig. 3c. The top of the β band is located at ~ 18 meV below E_F . Watson et al. have reported that the top of the β band is located at ~ 25 and 16 meV below E_F for the Γ and Z point, respectively¹². Therefore, k_z for 7 eV can be estimated to be closer to the Z point than the Γ point according to the results of Watson et al. As mentioned above, FeSe has been suggested to be in a BCS–BEC crossover regime⁴. The present result shows $E_F \sim 10$ meV for the α band (Fig. 3c). This corresponds to $\Delta/E_F \sim 0.2$ for the hole band at the BZ center. This is almost consistent with the previous report of $\Delta/E_F \sim 0.3$ from the STM/STS measurements⁴, which is smaller than the criteria of the BCS–BEC crossover regime, and should be an evidence that our results are reasonable and reliable. The electron band at the BZ corner might have $\Delta/E_F \sim 1$ and satisfy this criterion, as suggested from the STS/STM measurements⁴.

Figure 3d shows the E - k image below T_c (2 K) of cut #3 indicated in Fig. 3a, symmetrized with respect to E_F . This shows no detectable gap, which may demonstrate the existence of SC gap nodes. Figure 3f and g shows the EDCs at k_F and symmetrized EDCs with respect to E_F , respectively, taken with p -polarized light. Each EDC is identified with a FS angle θ , and the momentum positions in the FS are shown in Fig. 3e. Some of the symmetrized EDCs above T_c (15 K) seem to have a pseudogap. This might correspond to the preformed Cooper pairing associated with the BCS–BEC crossover regime reported by Kasahara et al.³⁰. They reported that the experimental signatures of the preformed Cooper pairing were observed below 20 K. It is clear from the spectra that the SC gap becomes smaller as θ reaches to 90° . Furthermore, the spectra around $\theta = 90^\circ$ show an undetectable gap, and thus, nodes may exist around $\theta = 90^\circ$. On the other hand, since the experimental observation limit is estimated to be ~ 0.2 meV, the SC gap minimum is at least smaller

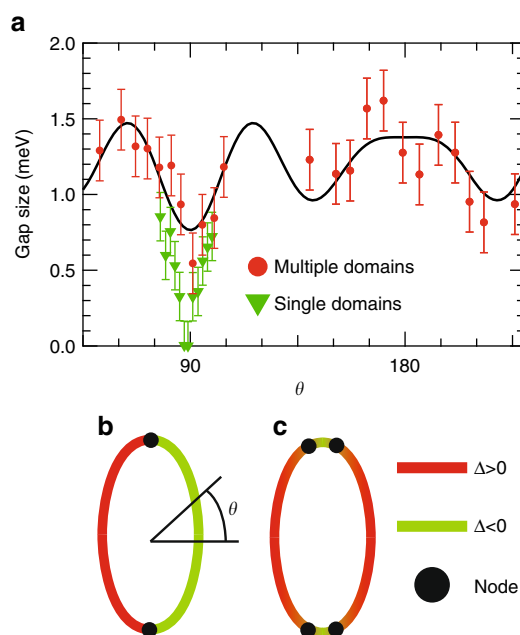


Fig. 5 Superconducting gap anisotropy of multi- and single-domain FeSe. **a** Superconducting gap anisotropy of the elliptical FS, shown in Cartesian coordinates. Results of the multi-domain samples (red circle) and single-domain samples (green triangle) are shown together. Error bars are determined by the systematic and statistical error of the calibrated E_F positions, as explained in Supplementary Note 8. The black curve is fitting to the observed anisotropy of the multi-domain samples, considering the twofold orthorhombic symmetry. The fitting function is $\Delta(\theta) = |A + B \cos(2\theta) + C \cos(4\theta) + D \cos(6\theta) + E \cos(8\theta)|$. Schematic description of gap signs on the Γ -centered FS assuming **b** a single node and **c** two nodes. The red (green) line indicates $\Delta > 0$ (< 0), and the black circles are the positions of nodes. Definition of θ is shown

than 0.2 meV. The BCS spectra fitting is shown in Fig. 3f, g as solid lines.

Figure 4 shows the obtained SC gap anisotropy. The results from the multi- and single-domain samples are shown together. For the multi-domain samples, the results with p - and s -polarized light are shown together, considering that each polarization shows a higher intensity for the domain rotated to each other by 90° . We fitted the results of the multi-domain samples to the following twofold symmetric formula of the summation of harmonic series:

$$\Delta(\theta) = |A + B \cos(2\theta) + C \cos(4\theta) + D \cos(6\theta) + E \cos(8\theta)|, \quad (1)$$

and the obtained fitting parameters were $A = 1.19$ meV, $B = 0.079$ meV, $C = 0.02$ meV, $D = 0.228$ meV, and $E = -0.141$ meV.

The observed SC gap anisotropy shows two major characteristics. First, it shows twofold symmetry. The orbital ordering makes the electronic structure twofold symmetric, and the SC gap anisotropy follows the symmetry. The SC gap at $\theta = 90^\circ$ shows a minimum, while that at $\theta = 0^\circ$ shows a maximum. This clearly demonstrates the breaking of the fourfold symmetry of the SC gap anisotropy. Fitting of the SC gap anisotropy also shows the breaking of the fourfold symmetry as well. Second, the observed SC gap anisotropy shows sharp anisotropy around $\theta = 90^\circ$. The gap shows a sharp drop toward $\theta = 90^\circ$. In contrast, the anisotropy becomes very weak around $\theta = 180^\circ$. These two observations show the necessity for considering the fourfold

symmetry breaking due to the orbital ordering when one pursues the mechanism of superconductivity in FeSe. Additionally, there are local minima around $\theta = \pm 45^\circ$ and $\pm 135^\circ$. The breaking of fourfold symmetry in SC gap anisotropy is basically consistent with very recent reports of ARPES on a similar compound $\text{FeSe}_{0.93}\text{S}_{0.07}$ ³¹, and Bogoliubov quasiparticle interference (BQPI) on FeSe³². Theoretically, twofold symmetry of SC gap anisotropy is explained based on spin fluctuations^{33,34}, cooperation between spin and orbital fluctuations³⁵, competition between nematic order and superconductivity³⁶, or orbital nematic fluctuations³⁷.

The observed SC gap anisotropy summarized in Fig. 5a shows a considerable difference between the multi- and single-domain samples. The results for the multi-domain samples show finite gaps at any θ , while those for the single-domain samples show an undetectable gap around $\theta = 90^\circ$. The difference of the SC gap size between the multi- and single-domain samples away from $\theta = 90^\circ$ becomes small and is almost within error bars at $\theta = 80^\circ$ and 100° .

Discussion

It is not likely that this different gap anisotropy is caused by the difference of disorder level among the pieces of samples. Teknowijoyo et al. have reported from the London penetration depth measurements that the gap minimum increases by ~ 0.05 meV after introducing point-like disorder by electron irradiation²⁴, when the created Frenkel pairs of interstitial vacancies are estimated to be $\sim 0.05\%$ per Fe and per Se (0.1% total pairs per formula). For our single crystals, the number of impurities and defects was confirmed to be $< 0.05\%$ per Fe by scanning tunneling microscope topography^{4,38}, and thus, the increase of the gap minimum due to impurities and defects is expected to be less than ~ 0.05 meV, which is much smaller than the difference of the gap minimum at $\theta = 90^\circ$ between the multi- and single-domain samples (~ 0.5 meV).

Alternatively, SC gap anisotropy could be affected by the existence of twin boundaries. According to Watashige et al., it has been suggested that twin boundaries induce a twist of the order parameter, and accordingly, time-reversal symmetry is broken and a fully gapped state is observed over a distance several times larger than the coherence length near twin boundaries³⁸. Because there should exist many twin boundaries within the laser spot for the multi-domain samples, the SC gap anisotropy for the multi-domain samples could reflect a fully gapped state due to time-reversal symmetry breaking. This could settle a contradiction between the different results for the thermal conductivity measurements. While Kasahara et al. observed a large κ_0/T (a residual linear term in the thermal conductivity as $T \rightarrow 0$ K) and suggested line nodes in the SC gap⁴, Bourgeois-Hope et al. observed a very small κ_0/T ²², although a residual resistivity is not significantly different between these two studies. This difference might be due to the density of twin boundaries. Moreover, the difference of the SC gap anisotropy between the multi- and single-domain samples around $\theta = 90^\circ$ is consistent with the theoretically calculated node disappearance due to time-reversal symmetry breaking³⁹. Therefore, the difference of the SC gap anisotropy between the multi- and single-domain samples is considered as the effect of time-reversal symmetry breaking near twin boundaries.

According to the SC gap determined from BQPI³², significantly anisotropic gap has been suggested for the zone-centered hole FS. Although the gap nodes were not observed by BQPI, since its reason might be due to the finite scanned area for the Fourier transform, our results should be totally consistent with the gap anisotropy determined from BQPI. If a single node is assumed at

the vertex, this means that a sign change occurs at each vertex of the major axis ($\theta = \pm 90^\circ$) as schematically shown in Fig. 5b. Although the signed values of the SC gap should become more continuous at $\theta = \pm 90^\circ$ in this case, the SC gap symmetry is considered to be a p -wave. This would be difficult to expect because there is no theoretical argument for p -wave pairing in this system and this seems inconsistent with the temperature dependence of the upper critical field^{40,41}. Thus, two nodes are assumed to exist at each vertex of the major axis ($\theta = \pm 90^\circ$) as shown in Fig. 5c, similar to KFe_2As_2 , which shows an octet-line node structure where two nodes exist within the narrow FS angle range²⁶. In this case, the sign changes occur twice around the vertices and the sign of the gap is consistent with the s -wave symmetry.

Methods

Sample preparation. High-quality single crystals were grown by the chemical vapor transport method using KCl/AlCl_3 as transport agent as described in ref. 3.

Laser-ARPES measurements. ARPES data were collected using a laser-ARPES apparatus at ISSP with 6.994 eV, sixth harmonics of Nd:YVO₄ quasi-continuous-wave (repetition rate = 960 MHz) laser, and VG-Scienta HR8000 electron analyzer as described in ref. 26. This apparatus achieves a maximum energy resolution of 70 μeV and the lowest cooling temperature of 1.5 K, which enables a direct measurement of the SC gap of FeSe. The overall energy resolution was set to ~ 1.2 meV and the angular resolution was 0.1° . The Fermi edge of an evaporated gold film was measured to calibrate E_F energy positions. The error bars of the SC gap size were determined from the stability of E_F position, and evaluated to be 200 μeV . More details for the accuracy of the measured gap size were described in the previous reports^{26,42}. Polarization of the incident excitation laser was adjusted using half-wave ($\lambda/2$) and quarter-wave ($\lambda/4$) plates. Samples were cleaved in situ under ultrahigh vacuum and measurements were carried out at pressures better than 5×10^{-11} Torr. The measurements were limited to the hole FS at the zone center due to the relatively low excitation energy of 6.994 eV, with which the momentum around the electron FS at the zone corner cannot be accessed.

Data availability. The data supporting the findings of this study are available from the corresponding author on request.

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Author contributions

T.H., Y.O., and H.Q.Y. performed the ARPES measurements. T.H. and K.O. analyzed the data. Y.S. and T. Shimojima designed a sample folder for the ARPES measurements on detwinned samples. S.W. and C.C. developed a VUV laser system. Samples were grown and characterized by S.K., Y.M., and T. Shibauchi. The manuscript was written by T.H., K.O., and S.S. All the authors discussed and contributed to the manuscript. K.O. and S.S. designed the project.

Additional information

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